

THE EFFECT OF SUBSTITUENTS UPON THE
DISSOCIATION OF HEXAARYLETHANES

BY

JULIUS FRANK KAPLAN

B.S., University of Illinois, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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OF ILLINOIS, 1941

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INTRODUCTION

Since Gomberg's¹ classical work on hexaphenylethane in 1900, several interesting theories have been advanced to explain the behavior of this type of compound. It has been found experimentally that none of the theories that have been advanced are completely satisfactory as an explanation for the dissociation of hexaarylethanes.

The purpose of this investigation is to prepare a series of hexaarylethanes substituted with alkyl groups in the *ortho*, *meta*, and *para* positions and to study the effects of these substituted alkyl groups on the degree of dissociation of the corresponding hexaarylethanes.

DISCUSSION OF RESULTS

The following hexaarylethanes have been prepared by the well known procedures^{2,3} and their degrees of dissociation have been measured by the magnetic susceptibility method⁴: hexa-*p*-ethylphenylethane ($17 \pm 2\%$), hexa-*p-n*-propylphenylethane ($21 \pm 2\%$), hexa-*p*-isopropylphenylethane ($26 \pm 2\%$), hexa-*p-n*-butylphenylethane ($23 \pm 5\%$), hexa-*p-sec*-butylphenylethane ($33 \pm 2\%$), hexa-*p*-isobutylphenylethane ($27 \pm 2\%$), hexa-*p-tert*-butylphenylethane ($28 \pm 5\%$), hexa-*p-tert*-amylphenylethane ($32 \pm 2\%$), hexa-*p*-cyclohexylphenylethane ($25 \pm 7\%$), hexa-*m*-tolylethane ($40 \pm 2\%$), di-*m*-tolyltetraphenylethane ($6.5 \pm 1\%$), di-*m-n*-amylphenyltetraphenylethane ($9 \pm 1\%$), di-*o*-tolyltetraphenylethane ($25 \pm 1\%$), di-*o*-ethylphenyltetraphenylethane ($33 \pm 2\%$), di-*p*-tolyltetraphenylethane ($5 \pm 1\%$), di-*p-n*-propylphenyltetraphenylethane ($6.5 \pm 1\%$), di-*p*-isopropylphenyltetraphenylethane ($8 \pm 2\%$), di-*p*-isobutylphenyltetraphenylethane ($7.5 \pm 1\%$), di-*p-sec*-butylphenyltetraphenylethane ($7.5 \pm 1\%$), di-*p-tert*-butylphenyltetraphenylethane ($7.5 \pm 2\%$), di-*p-tert*-amylphenyltetraphenylethane ($9 \pm 1\%$), tetra-*o*-tolylldiphenylethane ($82 \pm 2\%$), tetra-*m*-tolylldiphenylethane ($8 \pm 2\%$), tetra-*p*-tolylldiphenylethane ($5.5 \pm 1\%$), tetra-*p*-isopropylphenyldiphenylethane ($8 \pm 1\%$), tetra-*p-sec*-butylphenyldiphenylethane ($8.5 \pm 2\%$), tetra-*p-tert*-butylphenyldiphenylethane ($8.5 \pm 1\%$), tetra-*p-tert*-amylphenyldiphenylethane ($10 \pm 2\%$), di-*p*-tolyltetra-*p-tert*-butylphenylethane ($6 \pm 2\%$), tetra-*p*-tolyl-di-*p-tert*-butylphenylethane ($6 \pm 2\%$), di-*p*-tolyl-di-*p-tert*-butylphenyldiphenylethane ($7 \pm 2\%$), di-*p*-tolyl-di-*p*-ethylphenyldiphenylethane ($6 \pm 2\%$), di-*p*-tolyl-di-*p*-ethylphenyl-di-*p*-isopropylphenylethane ($10 \pm 2\%$).

It has been established that the dissociation of ethanes is influenced by the following factors: weight, size or steric hindrance, unsaturation and resonance. The dissociation of the above compounds can be explained as due to some of these factors or to a combination of the factors.

In the hexa-alkyl substituted ethanes there is a progressive increase in the degree of dissociation as the alkyl group increases from methyl to cyclohexyl. This increase can but be attributed to the increase in weight of the alkyl group. Similarly hexaalkylphenylethanes dissociate more than the corresponding dialkylphenyltetraphenylethanes. However, tetraalkylphenyldiphenylethanes have approximately the same degree of dissociation as the corresponding dialkylphenyltetraphenylethanes. This is true only for the compounds having *para* and *meta* substituents. This unusual behavior of the latter ethanes cannot be explained by any of the theories suggested to date on the dissociation of ethanes. It is, therefore, necessary to introduce a new factor of symmetry to explain the dissociations of these compounds. The higher dissociated compounds like the hexaalkylphenylethanes are in a symmetrical arrangement while the dialkylphenyltetraphenylethanes and the tetraalkylphenyldiphenylethanes are similar in their unsymmetrical arrangement.

In *ortho*-substituted compounds, however, the steric hindrance effect is so great that any symmetry effect is overbalanced. Likewise, steric hindrance is the factor which explains the increased effects upon the dissociation of hexaarylethanes when the alkyl groups are substituted in the *ortho* and to a smaller extent the *meta* positions.

Hexa-*p*-alkylphenylethanes in which the alkyl group has a hydrogen atom on the carbon atom attached to the ring have been found to dissociate to free radicals which undergo disproportionation. The di-*p*-alkylphenyltetraphenylethanes disproportionate less rapidly than the corresponding tetra-*p*-alkylphenyldiphenylethanes and they in turn disproportionate less rapidly than the corresponding hexa-*p*-alkylphenylethanes. A possible mechanism for the decomposition is proposed. The *tert*-butyl and the *tert*-amyl derivatives do not undergo disproportionation. Likewise, *ortho* and *meta* substituted alkyl ethanes are found to have very stable free radicals.

The *meta* and *ortho* alkyl substituted hexaarylethane solutions are lighter in color than the corresponding *para*-compounds, although their degrees of dissociation are higher than that of the *para* derivatives. The color of the free radical solution is therefore partly a characteristic of the groups present and their position and not of the degree of dissociation alone.

BIBLIOGRAPHY

¹ Gomberg, J. Am. Chem. Soc. **22**, 757 (1900).

² Moyer and Marvel, Organic Syntheses, Vol. **XI**, John Wiley and Sons, Inc., New York, N. Y., 1931, p. 98.

³ Copenhaver, Ph.D. Thesis, University of Illinois, 1935.

⁴ Roy, Ph.D Thesis, University of Illinois, 1937.

VITA

The writer was born in Chicago, Illinois, on June 2, 1912. He attended the public schools of that city, graduating from Bowen High School in June 1930. He entered Crane Junior College, receiving the two-year college degree in 1932. He continued his work at the University of Illinois in 1935 and received the degree of Bachelor of Science from that institution in 1937. He entered the Graduate School of the University of Illinois in February 1938. Since that time he has held an appointment as Assistant in Chemistry from September 1938 to February 1941.

